A PRELIMINARY INVESTIGATION ON THE PREMEABILITY OF PERMANENT GASES THROUGH FOAM MEMBRANES FOR GAS SEPARATIONS

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MASTER OF TECHNOLOGY

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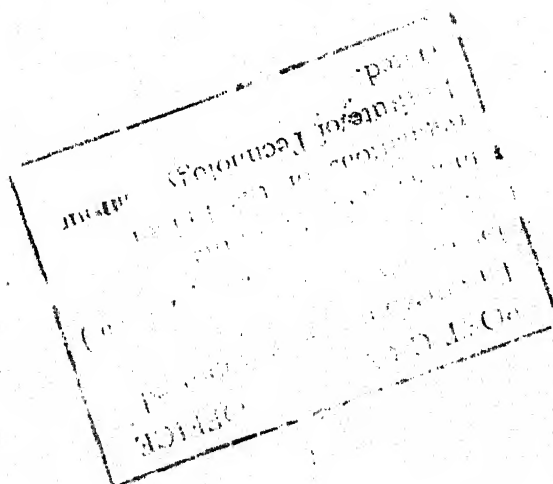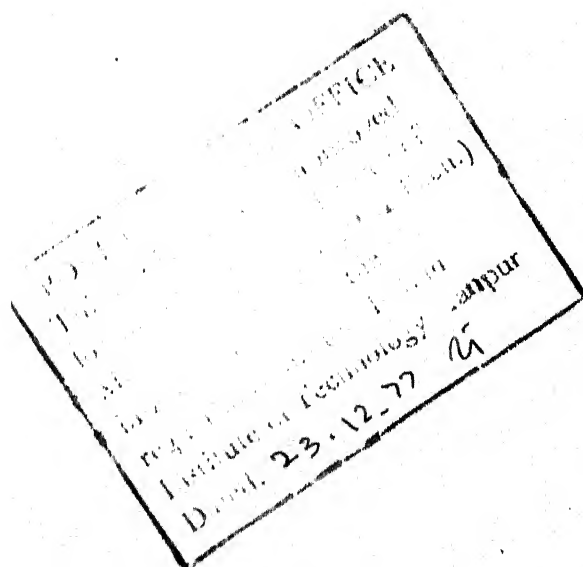**NOVEMBER 1977**

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CERTIFICATE

This is to certify that the present work 'A PRELIMINARY INVESTIGATION ON THE PERMEABILITY OF PERMANENT GASES THROUGH FOAM MEMBRANES FOR GAS SEPARATIONS' has been carried out under my supervision and has not been submitted elsewhere for a degree.

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ABSTRACT

Under conditions of permanent gases diffusing through foam bubble membranes with time dependent membrane surface area, a theoretical model for estimating gas permeabilities has been developed. For generating a monolayer of foam on the surface of a column of a liquid containing surfactants, an experimental glass apparatus has been fabricated. Experiments were conducted in this foam membrane permeator for O_2-N_2 and CO_2-O_2 systems to determine the permeabilities of individual gases as well as the separation factors $\alpha_{O_2-N_2}$ and $\alpha_{CO_2-N_2}$. The relevant quantities like average bubble diameter, bubble shrinkage with time due to unequal permeabilities etc., needed in the theoretical model to find out the permeability of the gases have also been measured. For O_2-N_2 system, three different compositions of the system glycerol – saponin-water were used by varying the glycerol content only and 70 per cent glycerol solution was found to generate the most stable foam.

The separation factors for the O_2-N_2 system were in the range of 1.7 to 5.8 with 70 per cent glycerol solution having separation factors always greater than 3.5 because of improved foam stability. These values are quite high and foam membrane separation of air is a distinct possibility. The separation factors for the CO_2-O_2 system were in the range of 6.7 to 8.3. These are somewhat lower than reported values due to possible absorption of CO_2.

CHAPTER 1

INTRODUCTION

Industrial separation of gases using membranes have recently generated considerable interest. Current applications invariably make use of a solid membrane along which the gas mixture to be separated flows at a high pressure and the permeating mixture of gases having a different composition is withdrawn downstream of the membrane at a low pressure. Solid membranes have several disadvantages. They have low gas permeabilities, and they are quite likely to have a few pin holes through which the feed gas mixture leaks to the permeate side without separation. In addition, capital investments are considerable while the operating costs are also high because of the high pressure differential needed to be maintained across the membrane thickness. A possible alternative to solid membranes is provided by liquid membranes which were developed by Li [1] in 1968 for the separation of liquid hydrocarbon mixtures. The liquid membrane in this case is essentially a thin aqueous layer containing surfactants, which encloses a drop of liquid hydrocarbon feed and which in turn is surrounded by another hydrocarbon medium of large extent into which some species from the encapsulated drop will preferentially permeate through the aqueous liquid membranes. There are several advantages of such liquid membranes, whether

aqueous or nonaqueous (in the latter case the droplet and the receiving medium are aqueous). Their thicknesses can be very small and since diffusivities in liquids are in general much higher than that in solids, the permeabilities are likely to be much higher if the gases are reasonably soluble. Further the separation factors are likely to be much higher than that in solid membranes because of wide differences in solubilities of various species in liquids [2]. Further liquid membranes do not have pin holes. On the other hand one cannot have a high pressure difference across the liquid membrane; In fact, the biggest single obstacle to the use of liquid membranes for gas separation is how to support the liquid membrane and provide a large surface area necessary for industrial level gas separations. Thus even though liquid membranes are about to become commercially successful [3], for separation of liquid mixtures because of the simpler techniques of emulsifying droplets of one liquid mixture in another receiving liquid with an intervening, immiscible liquid membrane such is not the case for separation of gaseous mixtures.

The earliest and the only reference to the use of a liquid membranes for the separation of a gas mixture is contained in the patent taken out by Li [4] in 1973. Li [4] separated mixtures of $1-C_4H_8$ and $2-C_4H_8$ by making a foam from a aqueous solution containing 70 per cent glycerol and 0.2 per cent saponin. The foam was carried up a column (of the

type normally used in foam fractionation) by a carrier gas (in this case N_2). As the foam rises up the column, driven by the surrounding carrier gas, the more permeable species will permeate at a higher rate through the aqueous surfactant layer into the carrier gas from which it can be separated later by absorption or liquefaction. It is obvious that in order to give sufficient contact time between the foam and the carrier gas the column has to be long and foam breakage becomes quite likely affecting the quality of separation. Further the carrier gas velocity cannot be very high so that output rate is quite low.

The motivating force behind this work is, to develop a foam membrane system for obtaining enriched air. Didwania[5] has already demonstrated the possibilities of an alternate way of using foam membrane system for gas separations by using foam in the form of a sheet carried down by a carrier liquid while exchanging gas with another carrier gas on the other side. In order to know what kind of separation is expected in such systems it was decided as a preliminary step to determine the permeabilities of these gases in a static apparatus using a foam membrane. Bulk of the investigations are intended for O_2-N_2 system which will provide more information for an air separation technique. The notable earlier investigation made in measurements of permeability of permanent gases, through flat surfactant films is that of R.L. Cook and R.W. Tock [6]

who used an aqueous film of 2 weight per cent Ivory liquid and 2 weight per cent Dupanol for the formation of liquid film. The driving force for enrichment was achieved by maintaining a temperature gradient across the aqueous surfactant film since the concept of foam seemed to have escaped their attention.

In this preliminary investigation an approximate mono-layer of foam is generated at the top of surface of a volume of liquid kept in a cylindrical glass container by bubbling a known volume of a gas species A through a sparger kept at the bottom of the liquid. The top of the liquid as well as the foam monolayer in the closed cylindrical vessel contains a second gas species B. The liquid membrane constituting the surfaces of the bubbles separates this second gas from the gas enclosed inside the bubbles constituting the foam. As time progresses, diffusion of the gas species B into the foam bubbles and diffusion of species A out of the foam bubbles take place. If the permeability of species A is more than that of the species B, the foam bubbles will shrink. One can simultaneously measure the decrease of height of individual foam bubbles with time as well as determine the composition of the gases in the enclosed gas space on top of the foam bubbles. Unlike the situation in dialysis with solid membranes whose surface area remains constant with time, this case is one of membranes surface area and shape varying with time. The method of determining permeability of individual gas species is therefore

quite different and difficult from that in dialysis for solute species dissolved in two liquid streams separated by a solid membrane. The objectives of this thesis are therefore primarily as follows:

1. Development of an appropriate analytical expression for predicting permeabilities from minimum measurements of concentration change and foam bubble height variation with time.

2. Make preliminary measurements of the required quantities in the following type of system: gas species A inside foam bubbles and gas species B outside with object of determining permeabilities of species A and species B and therefore the separation factor for A-B system with particular reference to the system O_2-N_2.

3. Obtain suitable information about foam stability as a function of the aqueous solution composition as well as about the nature of foam formed, the size distribution of foam bubbles etc. These informations are expected to provide an adequate guideline for designing and operating a continuous foam membrane separator for a gaseous mixture.

CHAPTER 2

MODEL FOR ESTIMATING GAS PERMEABILITY THROUGH FOAM MEMBRANES

In this chapter, a theoretical analysis of the bubble
shrinkage due to unequal permeabilities in a static foam
membrane, has been carried out and an appropriate analytical
expression, has been developed for predicting gas permeabilities
from measurable quantities like gas composition change, foam
bubble height variation with time, average bubble size etc.
As pointed out earlier, separation of gaseous mixtures
through foam membrane is similar to dialysis in many respects.
It is a rate governed membrane separation process. The
process is passive without any external forces like pressure
gradient or electrical potential gradient. No external
energy is required for the separation of gases. The driving
force for the diffusion of the gases is the concentration
 gradient maintained across the liquid foam membranes. The
problem of gas permeability determination with such an arrange-
ment is, however, much more complicated than dialysis, since
the surface area of the membranes is continuously changing with
time.

The system as shown in Figure 1, consists of a small
column with liquid upto the level H_1 from the bottom with the
space above being filled with a gas of volume V . At the surface
of the liquid a monolayer of foam is generated by bubbling
another gas, whose permeability through the liquid membrane

Gas B

6"

1

2

To Mano-
meter

To Orsat
Apparatus

3

Continuous phase

H_2

20"

H_1

Sparger

5

4

Feed liquid

Drain

6

To Vent
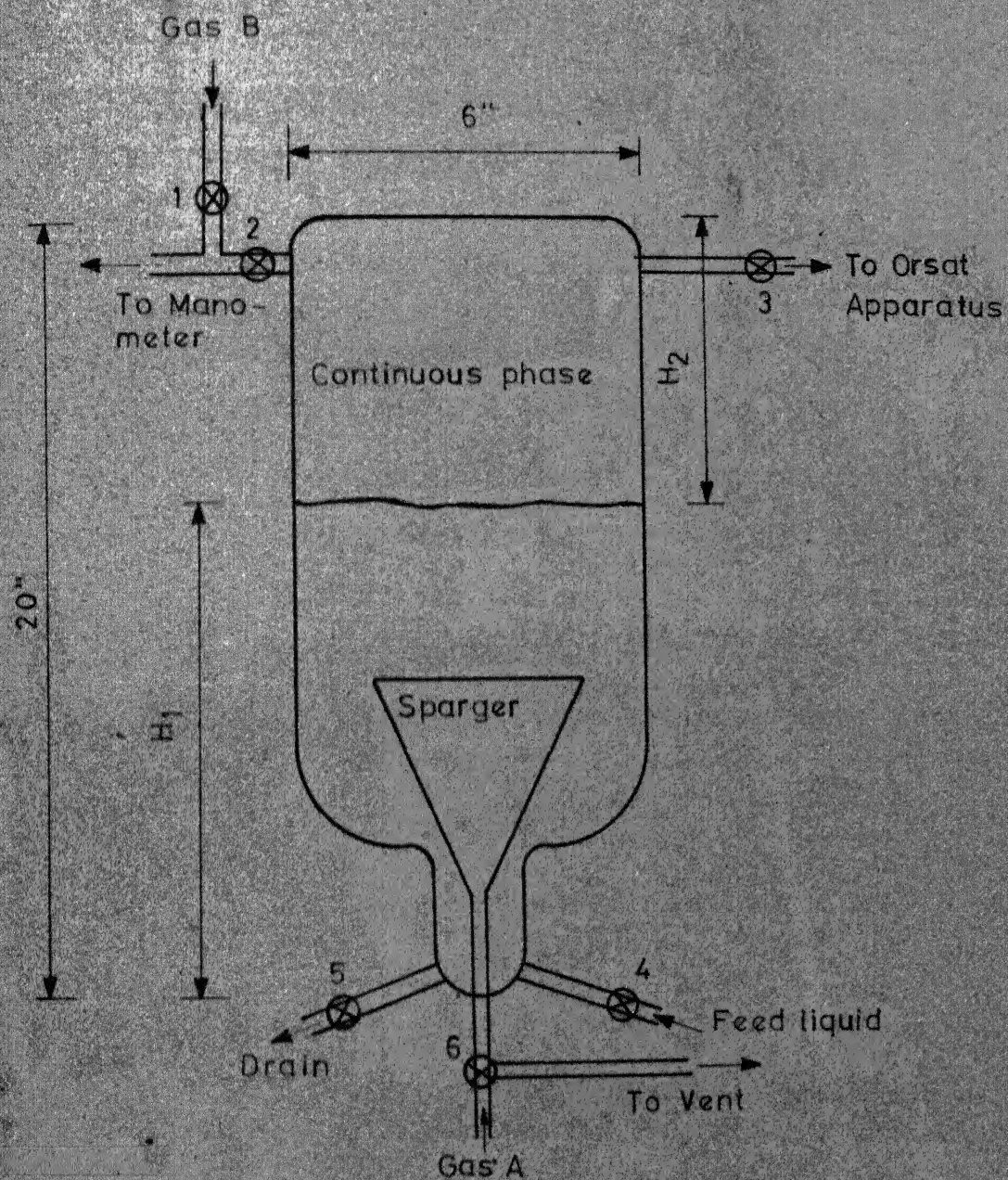
Gas A

FIG.1 APPARATUS FOR GENERATING FOAM MEMBRANES.

is to be determined along with that of the gas outside the foam. Initially the gas inside (gas A) and the gas outside the foam (gas B) are pure. As time proceeds, both gases permeate at different rates through the foam membranes it being assumed that the diffusional loss of species A into the liquid on which the foam stands is very little. This can be so only when the gases are sparingly soluble in the liquid. The species transfer process with time, leading to bubble shrinkage (if the gas A has higher permeability), can be described by the following equations:

From a material balance of gas species A and B,

$$\frac{dN_{AC}}{dt} = - \sum_{j=1}^{N} \frac{dn_{Aij}}{dt} \qquad (2.0A)$$

and

$$\frac{dN_{BC}}{dt} = - \sum_{j=1}^{N} \frac{dn_{Bij}}{dt} \qquad (2.0B)$$

where n_{Aij} = moles of species A inside jth bubble

n_{Bij} = moles of species B inside jth bubble

N_{AC} = moles of A outside the bubbles (continuous phase)

N_{BC} = moles of B in continuous phase

and N = total number of bubbles in the monolayer.

If the moles of species A and B inside all the bubbles are denoted by N_{Ai} and N_{Bi} respectively, the above equations become,

$$\frac{dN_{AC}}{dt} = - \frac{dN_{Ai}}{dt} \qquad (2.1)$$

and
$$\frac{dN_{BC}}{dt} = - \frac{dN_{Bi}}{dt} \qquad (2.2)$$

Since permeation of various gas species is assumed to be strictly due to concentration gradient, the mass flux through the liquid membrane around gas can be expressed in the form of Fick's first law, so that

$$\frac{dN_{Ai}}{dt} = \varepsilon \sum_{j=1}^{N} S_j \text{ Perm A } [\frac{N_{AC}}{N_{TC}} P_c - \frac{n_{Aij}}{n_{Tij}} P_{ij}] \qquad (2.3)$$

$$\frac{dN_{Bi}}{dt} = \varepsilon \sum_{j=1}^{N} S_j \text{ Perm B}[\frac{N_{BC}}{N_{TC}} P_c - \frac{n_{Bij}}{n_{Tij}} P_{ij}] \qquad (2.4)$$

where P_c = total pressure outside the membrane in the continuous phase

P_{ij}= pressure inside the jth bubble

S_j = surface area of the jth bubble

N_{TC} = total number of moles of gases in the continuous phase

n_{Tij}= total number of moles of all gases inside the jth bubble

Perm A = permeability of species A

and Perm B = permeability of species B

To solve the above equations (2.1), (2.2), (2.3) and (2.4), the following assumptions have been made:

(i) The gases are assumed to be ideal.

(ii) There is no bubble breakage (to prevent contamination).

(iii) There is very little absorption of either of
the gases in the liquid phase on which the foam
stands.

From the ideal gas law,

$$P_{ij} = \frac{n_{Tij} RT}{v_j}$$ (2.5)

and

$$P_c = \frac{N_{TC} RT}{N}{(V - \sum_{j=1}^{} v_j)}$$ (2.6)

where R = gas constant and

T = temperature

and v_j = volume of the jth bubble.

The excess pressure inside the bubble due to surface
tension can be written as,

$$P_{ij} - P_c = \frac{2\sigma}{r_j}$$ (2.7)

where σ = surface tension

r_j = radius of the jth bubble

Since this excess pressure is very small (see Appendix
A.2.1) it can be neglected in comparison to P_c. Therefore
equation (2.7) becomes

$$P_{ij} \cong P_c$$ (2.8)

If S_T denotes the total surface area of all the bubbles
through which species A and B simultaneously move in opposite
directions, equations (2.3) and (2.4) may be written as

$$\frac{dN_{Ai}}{dt} = \frac{N_{AC}}{N_{TC}} \, P_c \, \text{Perm } A \, S_T(t) - P_c \, \text{Perm } A \, \sum_{j=1}^{N} S_j(t) \frac{N_{Aij}}{n_{Tij}}$$

(2.9)

and
$$\frac{dN_{Bi}}{dt} = \frac{N_{BC}}{N_{TC}} \, P_c \, \text{perm } B \, S_T(t) - P_c \, \text{Perm } B \, \sum_{j=1}^{N} S_j(t) \frac{n_{Bii}}{n_{Tij}}$$

(2.10)

From (2.5), (2.6) and (2.8)

$$n_{Tij} = \frac{P_{ij} \, v_j(t)}{RT} = \frac{P_c \, v_j(t)}{RT}$$

and
$$N_{TC} = \frac{P_c \left(V - \sum_{j=1}^{N} v_j \right)}{RT}$$

Substituting these in (2.9) and (2.10), we have

$$\frac{dN_{Ai}}{dt} = \frac{[(RT \, \text{Perm } A) \, S_T] \, N_{AC}}{\left(V - \sum_{j=1}^{N} v_j \right)_I} - RT \, \text{Perm } A \, \sum_{j=1}^{N} \frac{S_j n_{Aij}}{v_j}_{II}$$

(2.11)

$$\frac{dN_{Bi}}{dt} = \frac{[(RT \, \text{Perm } B) \, S_T] \, N_{BC}}{\left(V - \sum_{j=1}^{N} v_j \right)} - RT \, \text{Perm } B \, \sum_{j=1}^{N} \frac{S_j \, n_{Bij}}{v_j}$$

(2.12)

If we write N_{Bi} as $Nn_{Ai}(t)$ and $N_{Bi} = N \, \bar{n}_{Bi}(t)$

$$\sum_{j=1}^{N} v_j = N \, \bar{v}(t), \qquad \sum_{j=1}^{N} S_j = N \bar{S}(t)$$

and
$$\sum_{j=1}^{N} \frac{S_j n_{Bij}}{v_j} \simeq N \frac{\bar{S} \, \bar{n}_{Bi}}{\bar{v}}$$
(even though this is not strictly true but is likely to be true for moderately dispersed size distribution).

where $\bar{n}_{Ai}$ = moles of A inside the average bubble

$\bar{n}_{Bi}$ = moles of B inside the average bubble

$\bar{v}$ = volume of an average bubble,

$\bar{S}$ = surface area of an average bubble.

Equations (2.1) and (2.2) can be written as,

$$\frac{dN_{AC}}{dt} = - N \frac{d\bar{n}_{Ai}}{dt} \qquad (2.13)$$

$$\frac{dN_{BC}}{dt} = - N \frac{d\bar{n}_{Bi}}{dt} \qquad (2.14)$$

Addition of (2.13) and (2.14) will yield,

$$\frac{dN_{TC}}{dt} = - N \frac{d\bar{n}_{Ti}}{dt} \qquad (2.15)$$

where $\bar{n}_{Ti} = \bar{n}_{Ai} + \bar{n}_{Bi}$ = total number of moles inside the

average bubble.

Integrating (2.13)

$N_{AC} + K = - N \bar{n}_{Ai} (t)$ where K is constant of integration

At $t = 0$, $N \bar{n}_{Ai}(t) = N^O_{Ai}$ which is equal to total moles of A

inside all the bubbles at time $t=0$.

Therefore $(N_{AC} - N^O_{Ai}) = - N\bar{n}_{Ai}(t)$ \qquad (2.16)

Similarly, we can get,

$$(N_{BC} - N^O_{BC}) = - N \bar{n}_{Bi}(t) \qquad (2.17)$$

$$(N^O_T - N_{TC}) = N \bar{n}_{Ti}(t) \qquad (2.18)$$

where N^O_{Bi} = total moles of B in continuous phase at time

$t = 0$

and N_T^O = total moles of A and B in the whole system at t=0.

For equation (2.11),

$$\text{Ratio I/II} = \frac{(RT \text{ Perm A}) \overset{N}{\underset{}{S_T}} N_{AC}}{(V - \overset{N}{\underset{j=1}{\varepsilon}} v_j)(RT \text{ Perm A}) N\bar{S} \, \bar{n}_{Ai}/\bar{v}}$$

$$= \frac{N\bar{v}}{(V - \overset{N}{\underset{j=1}{\varepsilon}} v_j)} \cdot \frac{N_{AC}}{(N_{Ai}^O - N_{AC})} \quad \text{(Substituting for } \bar{n}_{Ai} \text{ from (2.16))}$$

Here $N_{AC}/(N_{Ai}^O - N_{AC}) \cong 1$ for a very large time from t = 0

(see Appendix A.2.2).

Further if $V \gg N\bar{v}$, the term II in eqn. (2.11) is controlling.

Hence equation (2.11) may be simplified to

$$\frac{dN_{Ai}}{dt} = -RT \text{ Perm A} \overset{N}{\underset{j=1}{\varepsilon}} \frac{S_j \, n_{Aii}}{v_j} \quad (2.19)$$

Substituting for $-N\bar{n}_{Ai}(t)$ from (2.16)

$$\frac{dN_{AC}(t)}{dt} = \frac{RT \text{ Perm A}}{\bar{v}(t)/\bar{S}(t)} [N_{Ai}^O - N_{AC}(t)] \quad (2.20)$$

Solution of this equation for the initial condition t=0, $N_{AC}(t)$ = 0 and t=t, $N_{AC}(t)$=known, will enable us to determine Perm A. In practice, we have used known values of $\bar{v}(t)$, $\bar{S}(t)$, $N_{AC}(t)$ and $[d N_{AC}(t)/dt]$ at any given time to determine Perm A. The procedure for determining $\bar{v}(t)$ and $\bar{S}(t)$ from $\bar{r}$ and $\bar{h}(t)$ are given later in this section. The derivative is estimated from $N_{AC}(t)$ vs t data.

Since the gas is assumed to be behaving ideally,

$$p_{AC} = P_c \frac{N_{AC}}{N_{TC}} \quad ; \quad p_{BC} = P_c \frac{N_{BC}}{N_{TC}}$$

$$p_{Aij} = P_{ij} \frac{n_{Aij}}{n_{Tij}} \; ; \; p_{Bij} = p_{ij} \frac{n_{Bij}}{n_{Tij}}$$

where p stands for partial pressure.

Substituting these in equations (2.3) and (2.4)

$$\frac{N}{Perm\ A} \cdot \frac{d\bar{n}_{Ai}}{dt} = \sum_{j=1}^{N} S_j \, (p_{AC} - p_{Aij}) \qquad (2.21)$$

and

$$\frac{N}{Perm\ B} \frac{d\bar{n}_{Bi}}{dt} = \sum_{j=1}^{N} S_j \, (p_{BC} - p_{Bij}) \qquad (2.22)$$

Adding (2.21) and (2.22), we get

$$\frac{N}{Perm\ A} \frac{d\bar{n}_{Ai}}{dt} + \frac{N}{Perm\ B} \frac{d\bar{n}_{Bi}}{dt} = \sum_{j=1}^{N} S_j (p_{AC} + p_{BC} - (p_{Aij} + p_{Bij}))$$

$$= \sum_{j=1}^{N} S_j \, (P_c - P_{ij})$$

which on using relation (2.8) leads to

$$\frac{d\bar{n}_{Ai}}{dt} = -\frac{Perm\ A}{Perm\ B} \frac{d\bar{n}_{Bi}}{dt} \qquad (2.23)$$

From equations (2.5), (2.6) and (2.8) we get

$$\frac{n_{Tij}(t)}{v_j(t)} = \frac{\dfrac{N_{TC}}{N}}{V - \sum\limits_{j=1}^{N} v_j(t)}$$

Assuming $\dfrac{n_{Tij}(t)}{v_j(t)} = \dfrac{\bar{n}_{Ti}(t)}{\bar{v}(t)} = \dfrac{\dfrac{N_{TC}}{N}}{V - \sum\limits_{j=1}^{N} v_j}$

we obtain using (2.18),

$$\frac{\bar{n}_{Ti}(t)}{\bar{v}(t)} = \frac{\dfrac{N_T^o - N\bar{n}_{Ti}}{N}}{V - \sum\limits_{j=1}^{N} v_j}$$

$$\frac{\bar{n}_{Ti}(t)}{\bar{v}(t)} = \underbrace{\frac{N_T^O}{V - N\bar{v}(t)}}_{I} - \underbrace{\frac{N\bar{n}_{Ti}(t)}{V - N\bar{v}(t)}}_{II} \qquad (2.24)$$

The ratio of two terms on the right hand side of (2.24) is,

$$\frac{I}{II} = \frac{N_T^O}{N\bar{n}_{Ti}(t)}$$

if we assumed that $V \gg N\bar{v}$ as we have already done before obtaining (2.19); $N_T^O \gg N\bar{n}_{Ti}(t)$ so that the term II can be neglected in comparison to the term I. Therefore, equation (2.24) reduces to

$$\bar{n}_{Ti}(t) = \frac{N_T^O \cdot \bar{v}(t)}{V} \quad [\because \ V \gg N\bar{v}]$$

Thus $\bar{n}_{Ai}(t) + \bar{n}_{Bi}(t) = \frac{N_T^O \bar{v}(t)}{V}$ $\qquad (2.25)$

Differentiating this expression with respect to t, we get

$$\frac{d\bar{n}_{Ai}}{dt} + \frac{d\bar{n}_{Bi}}{dt} = \frac{N_T^O}{V} \frac{d\bar{v}}{dt} \qquad (2.26)$$

Substituting for $\frac{d\bar{n}_{Ai}}{dt}$ from (2.23) one obtains

$$\frac{d\bar{n}_{Bi}}{dt} = \left[\frac{Perm\ B}{Perm\ B - Perm\ A}\right] \frac{N_T^O}{V} \frac{d\bar{v}}{dt} \qquad (2.27)$$

Integration with respect to time leads to

$$\bar{n}_{Bi}(t) = \left[\frac{Perm\ B}{Perm\ B - Perm\ A}\right] \frac{N_T^O}{V} \bar{v}(t) + Constant.$$

At $t=0$, $\bar{n}_{Bi}(t) = 0$ and $\bar{v} = \bar{v}(0)$.

$$Constant = -\left[\frac{Perm\ B}{Perm\ B - Perm\ A}\right] \frac{N_T^O}{V} \bar{v}(0)$$

$$\bar{n}_{Bi}(t) = \left[\frac{Perm\ B}{Perm\ B - Perm\ A}\right] \frac{N_T^O}{V} [\bar{v}(t) - \bar{v}(0)] \qquad (2.28)$$

From (2.12)

$$\frac{N}{\text{Perm B}} \frac{d\bar{n}_{Bi}}{dt} = RT \left[\frac{N_{BC}}{V} N \bar{S}(t) - \frac{N\bar{n}_{Bi}(t) \bar{S}(t)}{\bar{v}(t)} \right] \quad (2.29)$$

$$\left(\text{since } V \gg \varepsilon \sum_{j=1}^{N} v_j \right)$$

$$\frac{1}{\text{Perm B}} \frac{d\bar{n}_{Bi}}{dt} = \frac{\bar{S}(t) RT}{V} \left[N_{BC} - \frac{V \bar{n}_{Bi}(t)}{\bar{v}(t)} \right]$$

But $N_{BC} = N_{BC}^O - N_{Bi}$

$$\frac{1}{\text{Perm B}} \frac{d\bar{n}_{Bi}}{dt} = \frac{\bar{S}(t) RT}{V} \left[N_{BC}^O - N_{Bi} - \frac{V\bar{n}_{Bi}(t)}{\bar{v}(t)} \right] \quad (2.30)$$

$$\left[\text{Since } N_{Bi} = N\bar{n}_{Bi} \right]$$

i.e.,

$$\frac{d\bar{n}_{Bi}}{dt} = \frac{RT \text{ Perm B}}{V} \bar{S}(t) \left[N_{BC}^O - \bar{n}_{Bi}(t)(N + \frac{V}{\bar{v}(t)}) \right]$$

Substituting for $\frac{d\bar{n}_{Bi}}{dt}$ and $\bar{n}_{Bi}(t)$ from (2.27) and (2.28) into this

$$\left[\frac{\text{perm B}}{\text{Perm B-Perm A}} \right] \frac{N_T^O}{V} \frac{d\bar{v}}{dt} = \frac{RT \text{ Perm B}}{V} \bar{S}(t) \left[N_{Bi}^O - \left[N + \frac{V}{\bar{v}(t)} \right] \times \right.$$

$$\left. \left[\frac{\text{Perm B}}{\text{Perm B - PermA}} \right] \frac{N_T^O}{V} (\bar{v}(t) - \bar{v}(0)) \right]$$

$$\quad (2.31)$$

$$\frac{d\bar{v}}{dt} = RT \bar{S}(t) \left[(\text{Perm B-PermA}) \frac{N_{BC}^O}{N_T^O} - \frac{(N + \frac{V}{\bar{v}})}{V} \text{ Perm B}(\bar{v}(t) - \bar{v}(0)) \right.$$

i.e.

$$\frac{d\bar{v}}{dt} = RT \bar{S}(t) \left[(\text{perm B-Perm A})x_B^O - \frac{(N + \frac{V}{\bar{v}})}{V} \text{Perm B}(\bar{v}(t) - \bar{v}(0)) \right]$$

$$\quad (2.32)$$

where $x_B^o = \dfrac{N_{BC}^o}{N_T^o}$.

i.e., $\dfrac{d\bar{v}}{dt} = RT\,\bar{S}(t)[(\text{Perm B}-\text{Perm A})x_B^o - \dfrac{1}{\bar{v}(t)}\ \text{Perm B}\ (\bar{v}(t)-\bar{v}(0))]$

(See Appendix 2.23)

i.e. $\dfrac{d\bar{v}}{dt} = RT\,\bar{S}(t)[(\text{perm B}-\text{perm A})x_B^o - \text{perm B}\ (1-\dfrac{\bar{v}(0)}{\bar{v}(t)})]$

(2.33)

The above equation can be solved to obtain perm B, knowing the initial conditions, the surface area and the volume of the bubble at any time t and perm A. This ordinary non-linear differential equation has been numerically solved after obtaining $\bar{v}(t)$ and $\bar{S}(t)$ as a function of $\bar{r}$ and $\bar{h}(t)$. The relationship between the surface area of an average bubble and its height $\bar{h}(t)$ as well as the radius of the bubble are dealt with next.

For calculating the volume and the curved surface area of the bubble, its shape must be known. The bubble shape as shown in Figure 2, is assumed to be that of an oblate spheroid for which the volume and surface area can be calculated [6] as follows:

The surface area of the average bubble is

$$\bar{S}(t) = \pi\,\bar{r}^2 + \dfrac{\pi}{2}\ \dfrac{\bar{h}^2(t)\bar{r}}{\sqrt{(\bar{r}^2-\bar{h}^2)}}\ \log_e \dfrac{\bar{r}+\sqrt{\bar{r}^2-\bar{h}^2}}{\bar{r}-\sqrt{\bar{r}^2-\bar{h}^2}}$$

(2.34)

where $\bar{r}$ = radius of the average bubble which is assumed to be constant.
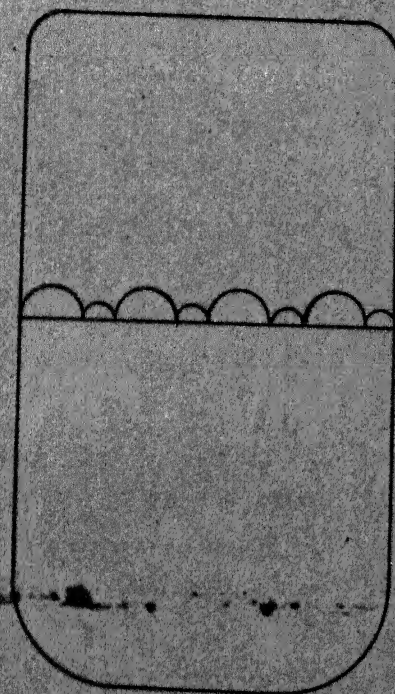
ELEVATION
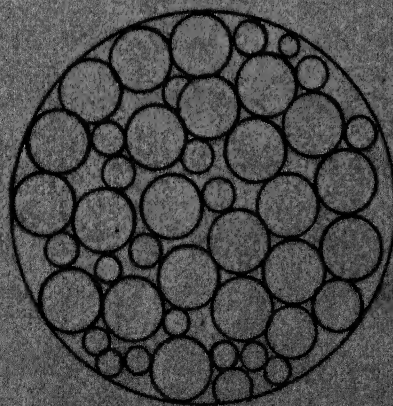
PLAN

FIG. 2 SCHEMATIC REPRESENTATION OF FOAM
BUBBLE MONOLAYER

$\bar{h}$ = height of the average bubble, which varies as

⌐ the gases diffuse through the bubble

The volume of the average bubble is given by

$$\bar{v}(t) = \frac{2}{3} \pi \, \bar{r}^2 \, \bar{h}(t) \tag{2.35}$$

Hence by measuring the radius and height of the bubble we can calculate the surface area and volume of the bubble at any time t. These values of the surface area and the bubble volume can be used to estimate $(d\bar{v}/dt)$ for use in the equation (2.33) for determining permeability of species B, since Perm A, $\bar{S}(t)$, $\bar{v}(0)$ and $\bar{v}(t)$ are known.

From the permeabilities of A and B which can be obtained from the equations (2.20) and (2.33) respectively, we can calculate the ideal separation factor which may be defined as

$$\text{Separation factor} = \frac{\text{Perm A}}{\text{Perm B}} \tag{2.36}$$

An absolutely rigorous procedure would have been to solve the nonlinear ordinary differential equation (2.33) for $\bar{h}(t)$ and also obtain an analytical solution for $N_{AC}(t)$ from (2.20). Since $\bar{h}(t)$ and $N_{AC}(t)$ are available experimentally, Perm A and Perm B could have been estimated.

The permeabilities of the gases which can be determined from the equations (2.20) and (2.33) are largely governed by the solubility of the gases in the foaming liquid. But it can be improved by adding a facilitating agent which enhances the permeation of one of the species [7]. The permeability values for the facilitated membrane has been given in Chapter 4.

CHAPTER 3

EXPERIMENTAL DETAILS

This chapter is divided into three sections. The first section deals with the chemicals used for the preparation of the foam membrane. The second section deals with the description of the experimental set up for gas permeability measurements and the third section explains the procedure used for taking data for the calculation of the permeability of gases A and B and the separation factor α_{AB}.

The steps followed during the course of experiment were as follows:

(i) Preparation of foaming liquid and filling the liquid in the glass column.

(ii) Formation of the foam membranes by bubbling gases through the sparger.

(iii) Measurement of the various factors used for the permeability calculation.

(iv) Breaking the foam membranes by draining the liquid and cleaning the apparatus with water.

3.1 Chemicals:

The chemicals needed for the preparation of the foaming liquid are glycerol, saponin, haemoglobin and water. Saponin acts as a surfactant for generating the foam. The glycerol used was a laboratory reagent grade while saponin

was of imported analytical reagent grade. The other chemicals needed were sodium dithionate and KOH for oxygen content measurement. Sodium sulphate, H_2SO_4 and methyl orange were used for the solution in the aspirator bottle of the Orsat gas analysis apparatus. For the absorption of oxygen 80 gms of sodium dithionate was dissolved in 40 ml of water. This was then mixed with 48 gms of KOH dissolved in 40 ml of water. The solution was shaken thoroughly before using for the absorption of O_2 in the Orsat apparatus. The solution used in the aspirator bottle consisted of 20 gms of aqueous sodium sulphate dissolved in 80 ml of H_2O and 4 gms of H_2SO_4. Methyl orange was used to give colour to the liquid.

3.2 Foam Membrane Permeator Details:

The design basis of the apparatus is available in Appendix A.3.1 at the end of this thesis. The apparatus (Figure 1) consisted of a corning glass-chamber of 6 inch diameter and 20 inch length. The chamber had a glass sparger of 5 inch diameter with 50 orifices of 1 mm diameter. The size of the orifices in the sparger had to be uniform to get bubbles of uniform dimensions. Through the stopcock (1), the chamber was connected to the gas cylinder containing gas B, while through the stopcock (2), the chamber was connected to the manometer filled with mercury. The gas to be analysed in the Orsat apparatus was taken through stopcock (3), which is a

two-way high vacuum stopcock. The foaming liquid kept in the feed bottle at a height H_2 to provide sufficient head for the flow of the liquid, was sent through the stopcock (4) while the draining had already been made through stopcock (5). The sparger kept inside the chamber was connected to a high vacuum three-way stopcock (6), the other two ways being connected to the vent line and the wet-test meter, which was connected to the gas cylinder containing gas A. The entire flow loop is shown in Figure 3.

3.3 Experimental Procedure:

The foaming liquid was prepared with various concentrations of glycerol to find out the effect of liquid composition on separation factor. It is assumed that increased glycerol concentration will make the foam stabler since Li's [4] liquid membrane stability increased very much with increase in glycerol content. For O_2-N_2 system, the concentration of the foaming liquid used were:

(i) 30 per cent glycerol, 68 per cent H_2O and 2 per cent saponin.

(ii) 50 per cent glycerol, 48 per cent H_2O and 2 per cent saponin.

(iii) 70 per cent glycerol, 28 per cent H_2O and 2 per cent saponin. (without facilitating agent)

(iv) 70 per cent glycerol, 28 per cent H_2O and 2 per cent saponin (with Haemoglobin acting as a facilitating agent).
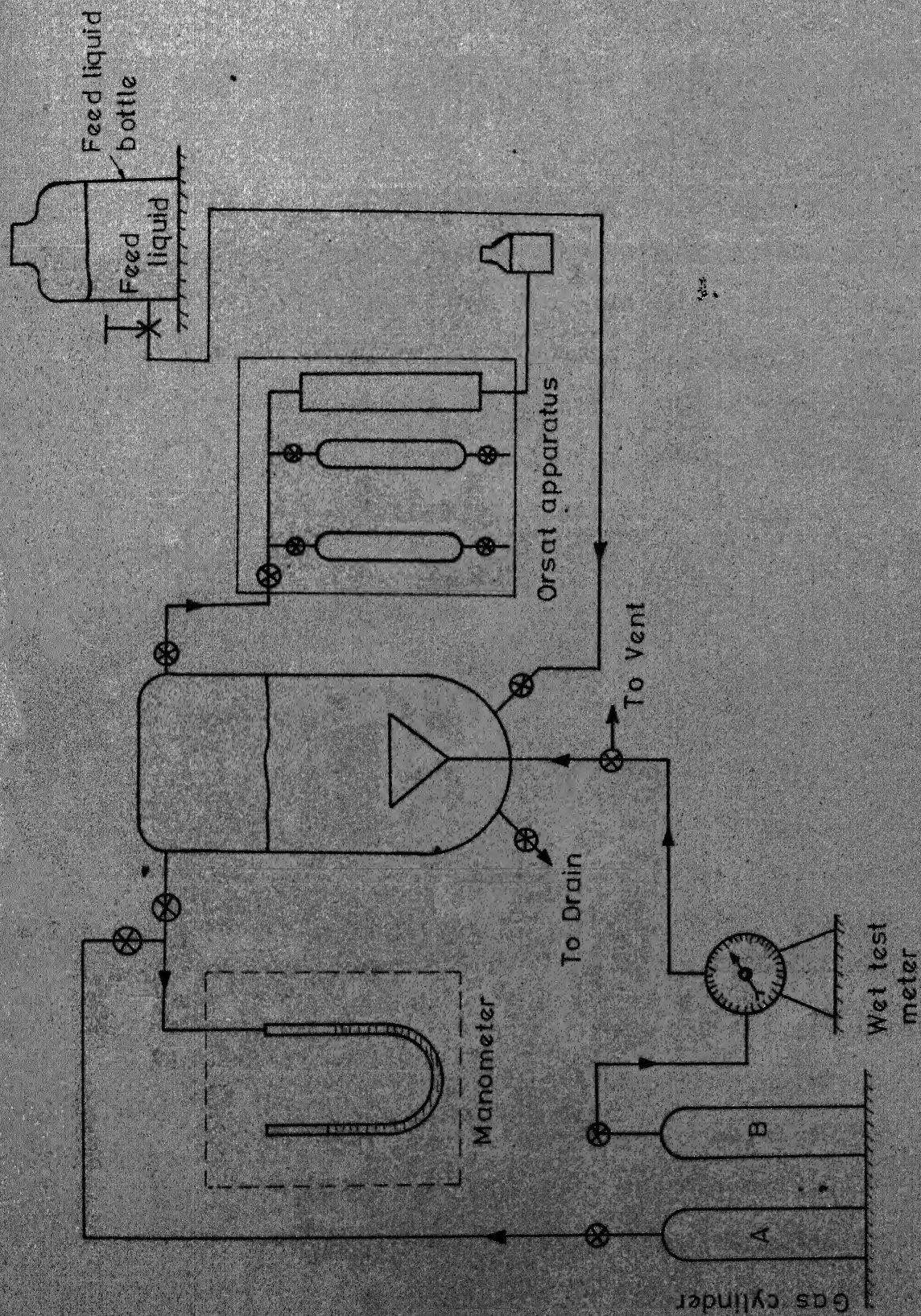
FIG.3 SCHEMATIC DIAGRAM OF THE EXPERIMENTAL APPARATUS.

For CO_2-O_2 system the liquid used was

      70 per cent glycerol, 28 per cent H_2O and 2 per
      cent saponin.

Foaming liquid thus prepared was fed into the chamber from the feed bottle shown in Figure 3. Sufficient space was provided at the top of the foaming liquid in accordance with the assumption $V \gg n\bar{v}$, made in the development of theoretical equations in Chapter 2. The space above the liquid was filled with gas B, sent through stopcock (1), after flushing the space with gas B. Minimum pressure (about 1.01 atms) had been kept at this space to minimise breakage of bubble during the bubble forming process. The system was ready for operation under such conditions. A monolayer of the foam of gas A was formed on top of the foaming liquid, by slowly sending the gas A through the sparger which in turn was connected to the wet-test meter. Because of the higher permeability of gas A, the foam bubble started shrinking with time immediately. The various quantities needed for the calculation of permeabilities of gas A and B (and hence separation factor) are: (a) total moles of gas B initially present, (b) total moles of gas A supplied for making foam (assuming no loss); (c) the average radius of the bubble, (d) height of any shrinking foam bubble as a function of time; (e) radius of the bubble for which the reduction in

height was measured; (f) composition of the gases in the
continuous phase at various times, as it changed due to the
permeation of A and B through the foam membrane.

Total moles of gas A at time t=0 was obtained by noting
the pressure in the continuous phase and the volume of the gas
space above the foaming liquid. The pressure was noted with
the help of a manometer attached to stopcock (2), while the
volume was calculated from the height of the gas space and
the radius of the chamber which were measured. The total
moles of gas B at time t=0 was obtained from the pressure and
the volume of the gas fed in through the sparger. The volume
of the gas A fed in was obtained from the wet-test meter, while
the pressure was noted from the manometer connected to it.
The average radius of the bubbles was obtained by photographing
bubbles formed on the top of the foaming liquid. The total
number of bubbles in a particular area of the photograph was
counted to get the size of the average bubble. The height
of the bubble at various interval of time was measured by
focussing the bubble to the crosswire intersection of a catheto-
meter. Every minute the crosswire intersection was made to
coincide with the tip of the bubble and the corresponding
reading was taken from the scale attached to the cathetometer.
The radius of the bubble for which the height reduction was
noted was obtained from the angle of the arc and the radius
of the arc of the circle to which the diameter of the bubble

was the chord. The angle was measured with the scale provided at the bottom of the cathetometer. The radius of the arc, which was the distance of the bubble to its image in the eyepiece, was obtained by focussing an object without disturbing the eyepiece and measuring its distance from the image. From the angle and the radius of the arc, the chord length was calculated. This was the diameter of the bubble. Composition of the gases in the continuous phase was measured by taking 75 cc of the gas from the continuous phase and analysing it with the help of Orsat apparatus. From the reduction in volume of the gases in the gas measuring burette of the Orsat apparatus after absorption of one of the two species in the continuous phase, the percentage by volume of species A and B was calculated. Since volume per cent = mole per cent, these values were substituted in the equation (2.20) for the calculation permeability A.

CHAPTER 4

RESULTS AND DISCUSSION

.In this chapter, the results of the experiments carried out to determine the permeability of gases through foam liquid membranes have been presented. Experiments were conducted primarily for the O_2-N_2 system with various compositions of the water-glycerol saponin foaming liquid. A few runs were made with the CO_2-O_2 system also. The system O_2-N_2 is important for separation problem and therefore extra emphasis was put on it to the exclusion of the other systems. Due to the nonavailability of large number of permanent gases and the difficulty in analysing the compositions of such gases, only limited data with limited number of other systems could be taken. The results of the experiment conducted for the O_2-N_2 system with 30 per cent glycerol solution are not reported here since the extent of foam breakage was found to be large because of higher foam drainage rate with low viscosity solutions.

The results are presented under the following headings:

(i) Effect of liquid composition on foam stability

(ii) The nature of foam bubbles

(iii) The variation of foam bubble height with time.

(iv) Determination of gas permeabilities.

(i) <u>Foam Stability:</u> Visual observations of monolayer foams

produced in the experiments indicated that as the glycerine
concentration increases the foam stability increases. Rough
counting of the number of foam bubbles breaking in a given
interval of time was done and as the glycerin content of the
2 per cent saponin solution in water increased from 30 per cent
by weight to 70 per cent by weight, bubble breakage became a
rare event. Only three compositions were used: 30 per cent,
50 per cent and 70 per cent glycerol by weight. Experiments in
the higher concentration of glycerol could not be carried out
since the handling of the solution posed a serious problem with
highly stable foams being generated during any transfer operation
between reservoirs. The stability was in general independent
of the bubble sizes except in the case of very small bubbles
having diameters around 0.20 cm. These were much more stable
than the bigger ones with even 30 per cent glycerol solution.
(ii) <u>Nature of Foam Bubbles</u>: A schematic diagram depicting
the actual nature of foam bubbles from a position right above
them is shown in Figure 2. A photograph of the bubbles is also
attached herewith (Figure 4A). It may be noticed that the
bubbles less than 2 cm in diameter but greater than 0.6 cm. The
others had size ranging between 0.6 cm and 0.1 cm. However,
their total surface area was almost always less than 5 per cent
of the total surface area of the bubbles. No attempt was made
to study the height reduction of such tiny bubbles. Visual study
of the bubbles further revealed that initially (t=0) most of
the bubbles were of hemispherical shape. There is always some

FIGURE 4a: PHOTOGRAPH OF THE BUBBLES

coalecence at the beginning of each experiment. As time progressed, it changed to a form similar to an oblate spheroid with the height reduced. This supports the assumptions made in Chapter 2.

3. <u>Variation of Foam Bubble Height with Time</u>: In Figures 4,5,6 and the 7 the variation with time of the height of several foam bubbles are shown. In anyone of these figures, the height variation with time for a particular bubble is very rapid in the initial period, but becomes almost zero at a large time. In so far as height variation with time is indicative of the separation process, obviously the rate of separation decreases with increasing time since the concentration driving force decreases with the concentration of A increasing outside the bubbles. It may be pointed out also that even though anyone of the figures 4,5,6 and 7 contain a number of curves for different sized bubbles, only one curve can be generated in a given experiment due to the limitations of one observer and one cathetometer. However, experiments were repeated under conceivably identical conditions for any particular system and the height variation of a similar bubble was noted against time. Since the curves in a given Figure (e.g. Fig. 4 or Fig 5 or Fig. 6) are for bubbles with different size and the theory for this work as pointed out in Chapter 2 requires the height variation of an average bubble whose size is estimated from photographs, the height variation with time of such an average bubble has been obtained by Lagrangian interpolation formulae [9] (see Appendix A.4.1) and tabulated in Tables 4.1, 4.2, 4.3 and 4.4.

FIG. 4

BUBBLE HEIGHT VARIATION WITH TIME FOR O_2-N_2 SYSTEM
(50 % Glycerol)

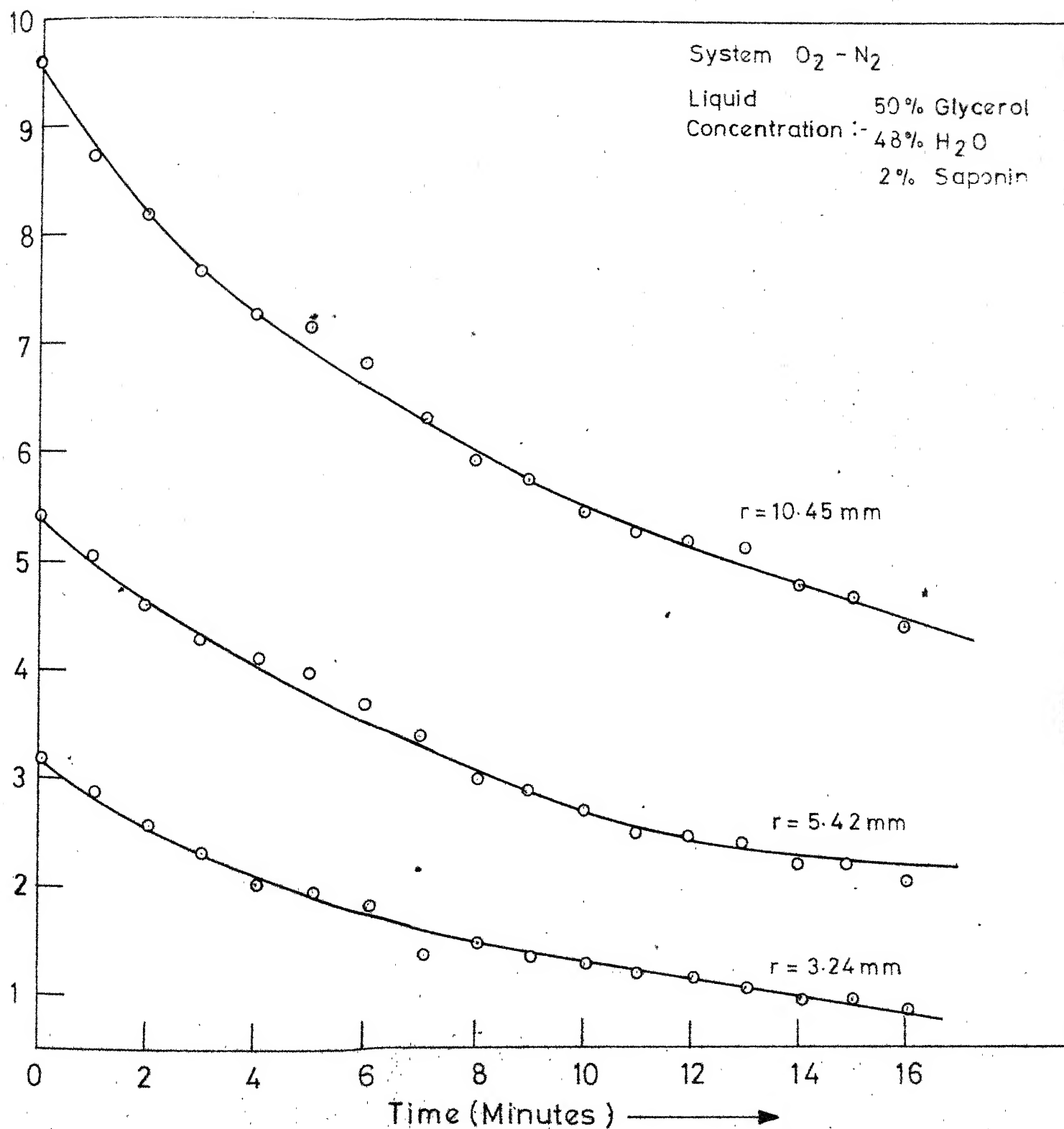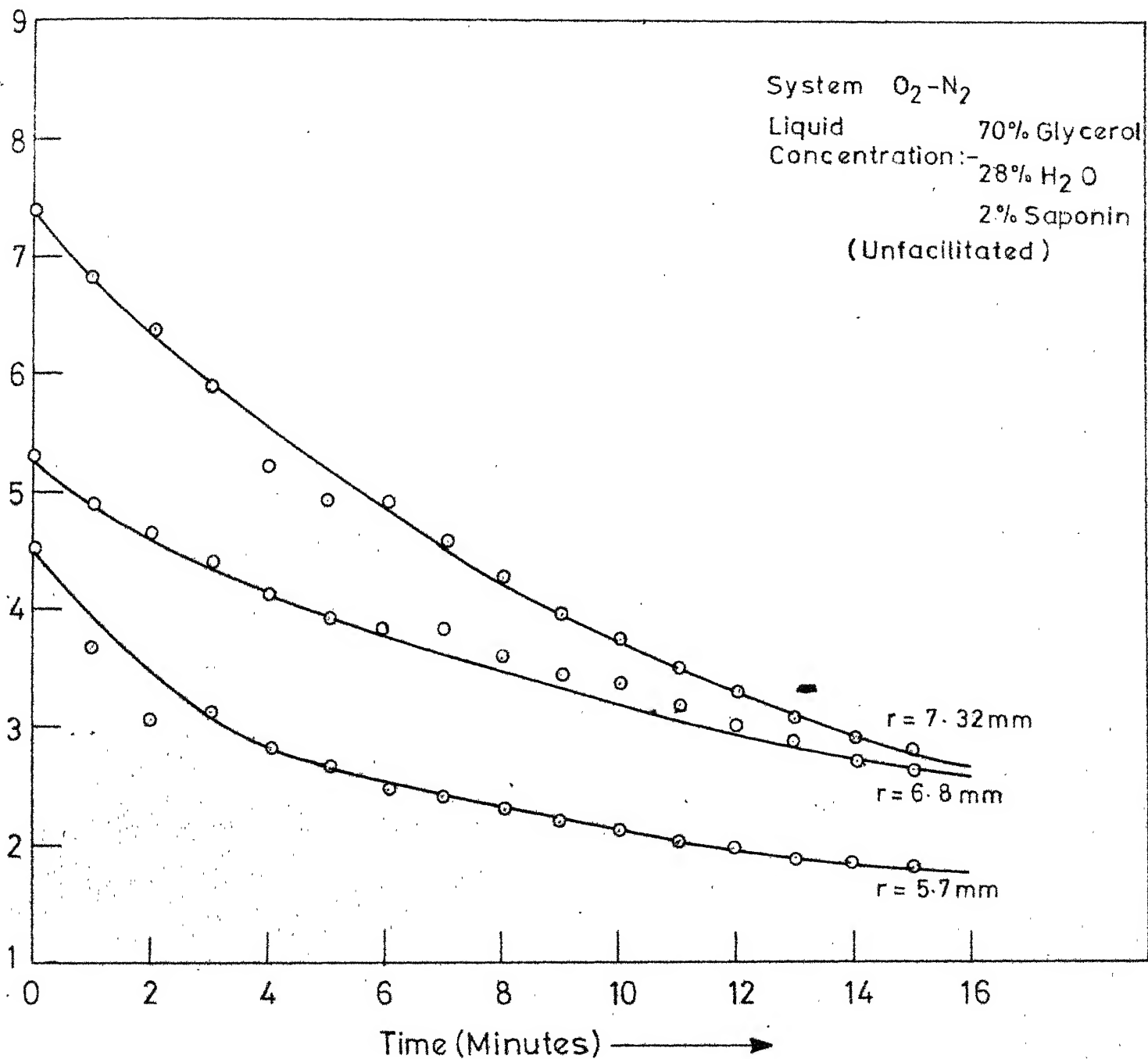FIG.5

BUBBLE HEIGHT VARIATION WITH TIME FOR O_2-N_2 SYSTEM
(70% Glycerol)
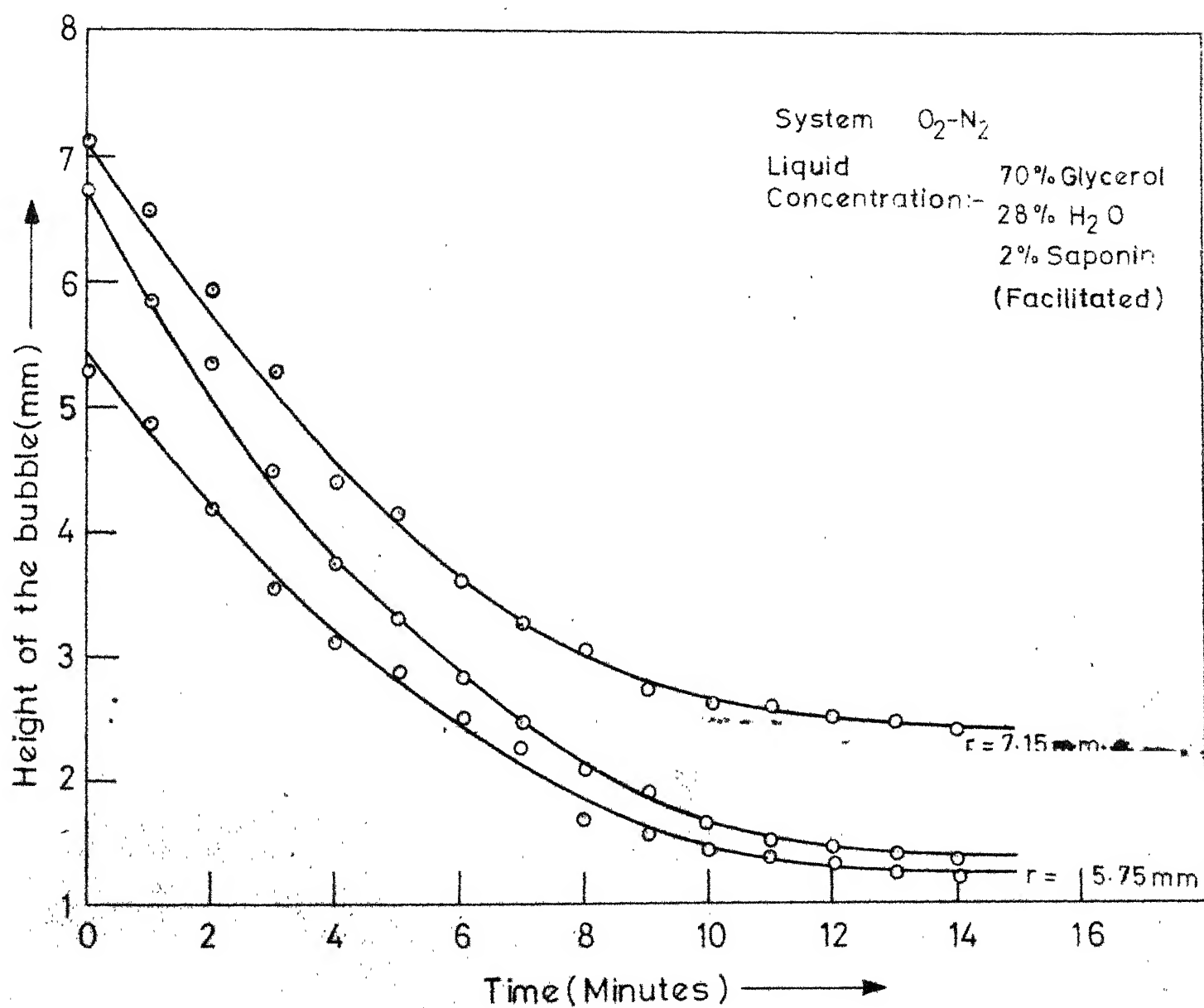
FIG. 6

BUBBLE HEIGHT VARIATION WITH TIME FOR O_2-N_2 SYSTEM
(70% Glycerol) O_2 Transport facilitated

System: $CO_2 - O_2$

Liquid Concentra- tion
70% Glycerol
28% H_2O
2% Saponin

r = 0.51 mm

r = 0.375 m m

r = 0.330 mm

Time (Minutes) ⟶
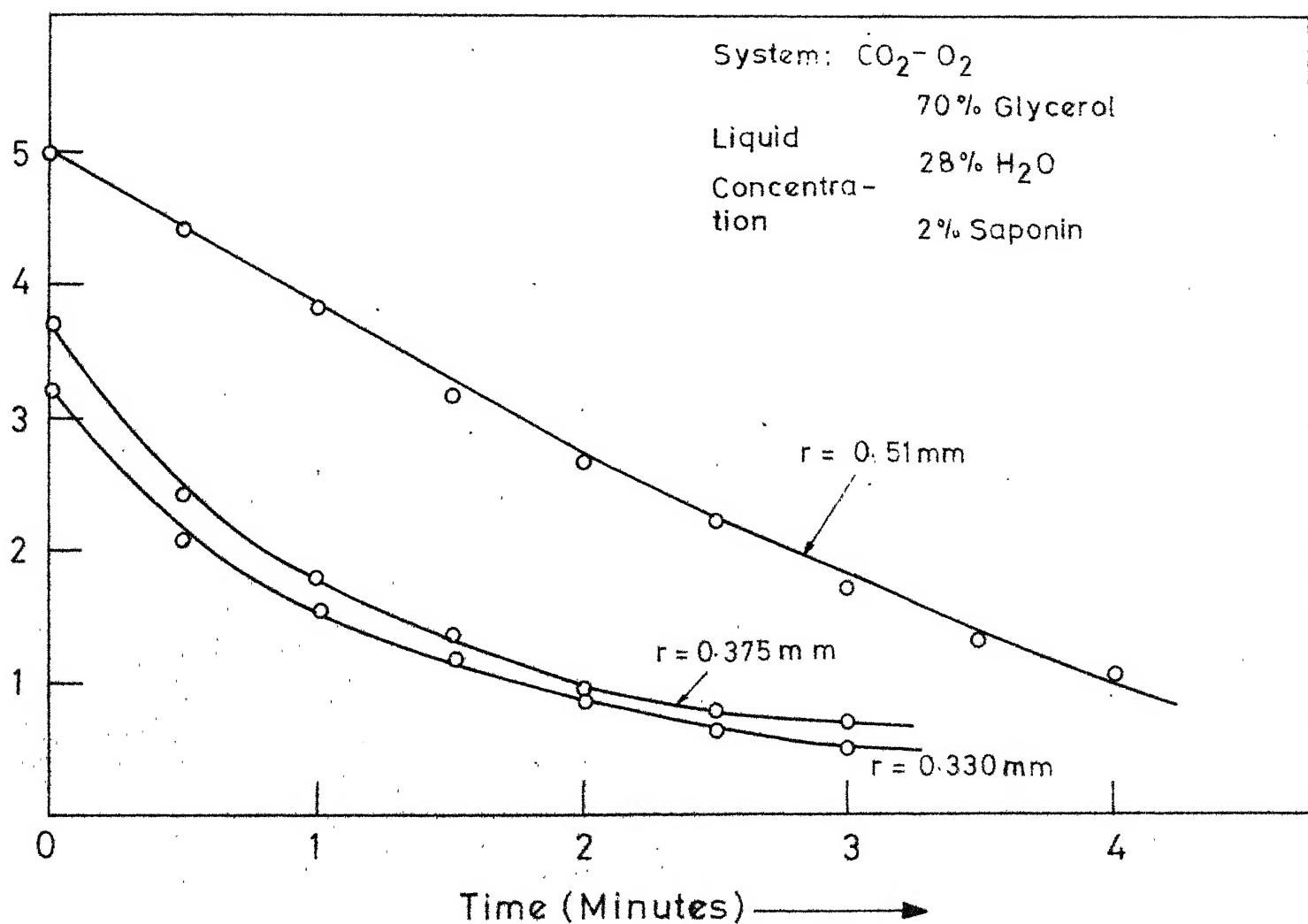
FIG. 7

HEIGHT VARIATION WITH TIME FOR $CO_2 = O_2$ SYSTEM (70% Glyce-

SYSTEM O_2-N_2

Height of the column above
bubble surface = 18.2 cm

Volume of O_2 sent in = 400 cc

Pressure P_c = 1.022 atm

Average bubble radius $\bar{r}$ = 0.371 cm

Time, min.	Bubble height/Radius (cm) $h_1/0.324$	$h_2/0.542$	$h_3/1.045$	Average bubble ht.in cm.	Composition of O_2 per cent	Volume of average bubble $\bar{v}$ cc	Surface area of average bubble $\bar{s}$ cm.	Perm A×10⁶ gm.moles/ cm².atm.min	Perm B×10⁶ gm.moles/ cm².atm.min
0	0.320	0.540	0.960	0.3685	0	0.1362			
1	0.285	0.500	0.880	0.3331					
2	0.255	0.465	0.825	0.3023					
3	0.230	0.435	0.775	0.2765					
4	0.210	0.405	0.730	0.2542	6.5	0.0797	0.0797	2.8	1.6
5	0.190	0.380	0.695	0.2331					
6	0.170	0.355	0.665	0.2120				$\alpha_{AB}=1.687$	
7	0.160	0.330	0.635	0.1981					
8	0.145	0.308	0.605	0.1813	7.03	0.0523	0.5914		
9	0.138	0.288	0.580	0.1705					
10	0.130	0.270	0.550	0.1608					
11	0.123	0.255	0.535	0.1512					
12	0.115	0.243	0.515	0.1426	7.42	0.0411	0.5436		
13	0.110	0.235	0.495	0.1373					
14	0.100	0.225	0.480	0.1274	7.85	0.0367	0.5278		
15	0.090	0.220	0.460	0.1192					

TABLE 4.1: O_2-N_2 SEPARATION THROUGH 50 PER CENT GLYCEROL FOAM LAMELLAE

SYSTEM O_2-N_2

Height of the column above the liquid surface H_z = 18.2 cm   Volume of O_2 sent in = 500 cc

Pressure, P_c = 1.022 atm   Pressure P_{ij} = 1.022

Radius of the average bubble $\bar{r}$ = 0.596 cm

Time, min.	Bubble Height/Radius (cms)			Ht. of average bubble by interpolating $\bar{h}$ cms	Composition of O_2 per cent	Vol. of average bubble $\bar{v}$ cc	Surface area of average bubble $\bar{S}$ cm²	Perm Ax10⁶ $\frac{gm.moles}{cm^2 min.atm.}$	Perm B x 10⁶ $\frac{gm.moles}{cm^2 min.atm.}$
	$h_1/0.570$	$h_2/0.68$	$h_3/0.732$						
0	0.450	0.525	0.730	0.4230	0	0.3147			
1	0.385	0.490	0.680	0.3735					
2	0.340	0.460	0.630	0.3388					
3	0.310	0.440	0.590	0.3178	6.78	0.2364	1.5816	1.2	0.344
4	0.285	0.415	0.550	0.2967					
5	0.265	0.395	0.513	0.2727					
6	0.255	0.380	0.485	0.2630					
7	0.240	0.365	0.455	0.2616					
8	0.230	0.345	0.425	0.2518					
9	0.225	0.330	0.395	0.2458					
10	0.215	0.315	0.375	0.2354					
11	0.205	0.305	0.350	0.2293					
12	0.200	0.295	0.330	0.2250	10.89	0.1674	1.3970		
13	0.190	0.285	0.310	0.2176					
14	0.183	0.275	0.295	0.2114					
15	0.175	0.265	0.280	0.2035	11.80	0.1514	1.3560	3.9	0.674

$\alpha_{AB}=3.488$

$\alpha_{AB}=5.78$

TABLE 4.2: O_2-N_2 SEPARATION THROUGH 70 PER CENT GLYCEROL FOAM MEMBRANES

SYSTEM O_2-N_2

Height of the gas space above liquid level = 18.2 cm Volume of O_2 sent = 500 cc

Pressure, P_c = 1.022 atm Average bubble radius $\bar{r}$ = 0.582 cm

Time, min.	Bubble height/Radius(cms)			Ht. of average bubble $\bar{h}$ cms	Composition of O_2 per cent	Vol. of average bubble $\bar{v}$ (cc)	Surface area of average bubble $\bar{S}$ cm²	Perm A x10⁶ gm.moles cm² min. atm.	Perm B x10⁶ gm.moles cm² min atm
	h_1/0.576	h_2/0.675	h_3/0.715						
0	0.545	0.670	0.705	0.5563	0	0.3947			
1	0.480	0.580	0.635	0.4854					
2	0.420	0.500	0.575	0.4208					
3	0.365	0.435	0.510	0.3649	3.8	0.2589	1.184	1.0	0.6648
4	0.320	0.380	0.475	0.3172					
5	0.280	0.330	0.405	0.2774				$\alpha_{AB}=1.5042$	
6	0.240	0.290	0.360	0.2379					
7	0.210	0.250	0.328	0.2059					
8	0.180	0.215	0.300	0.1745					
9	0.160	0.185	0.280	0.1520					
10	0.145	0.165	0.270	0.1353					
11	0.135	0.155	0.260	0.1253	8.3	0.1238	1.2522		
12	0.130	0.145	0.250	0.1252					
13	0.128	0.140	0.245	0.1175	11.3	0.0960	1.1903	4.7	0.950
14	0.125	0.138	0.240	0.1147					
15	0.125	0.135	0.240	0.1141				α_{AB} = 4.94	

TABLE 4.3: O_2-N_2 SEPARATION THROUGH 70 PER CENT GLYCEROL FOAM MEMBRANES - O_2 TRANSPORT FACILITATED.

SYSTEM CO_2-O_2

Height of the gas space above bubble surface = 18.2 cm Volume of O_2 sent = 500 cc

Pressure in conti-phase P_c = 1.022 atm Average bubble surface radius $\bar{r}$ = 0.405 cm

Time, min	Bubble height/Radius cm			Ht. of average bubble $\bar{h}$ cms	Composition of O_2 per cent	Vol. of average bubble $\bar{v}$ cc	Surface area of avg. bubble $\bar{S}$ cm²	Surface Perm×10^6 $\frac{gm.moles}{(cm^2)(min) atm.}$	Perm B×10^6 $\frac{(gm.moles)}{(cm^2)(min) atm.}$
	h_1/0.51	h_2/0.375	h_3/0.330						
0	0.496	0.368	0.320	0.399	0	0.1370			
0.5	0.439	0.250	0.215	0.281	4.1	0.0960	0.832	60	7.3
1.0	0.385	0.175	0.155	0.203				α_{AB}=8.219	
1.5	0.330	0.135	0.117	0.197					
2.0	0.275	0.100	0.085	0.123	8.02	0.0430	0.609		
3.0	0.185	0.070	0.055	0.087					
3.5	0.140	0.070	0.050	0.085	9.1	0.0230	0.565	75.3	11.29

$\alpha_{AB} = 6.67$

TABLE 4.4: CO_2-O_2 SEPARATION THROUGH 70 PER CENT GLYCEROL FOAM MEMBRANES

(iv).<u>Determination of Gas Permeabilities</u>:

The various data needed for the gas permeability calculations are tabulated in Tables 4.1, 4.2, 4.3 and 4.4. These quantities were substituted in equations (2.20), (2.34), (2.35) and (2.36) and solved numerically to determine Perm A and Perm B. A model calculation for determining gas permeabilities as well as the separation factor α_{AB} is shown in Appendix (A.4.2). The results are tabulated in Tables 4.1, 4.2, 4.3 and 4.4.

A look at Tables 4.1, 4.2, and 4.3 shows that the separation factor α_{AB} for the oxygen (A) - Nitrogen (B) system increases general with (1) increase in glycerol concentration and (2) with time. Further the separation factor values are in the range 3.4 to 5.8 with 70 per cent glycerol solution. In addition, the introduction of haemoglobin, a known O_2-facilitating agent, does not substantially increase the separation factor with is quite unusual. The explanation for this type of results are to be sought from the experimental observations, nature of data reduction and the numerical solution techniques adopted.

The addition of 0.3 per cent haemoglobin to the 70 per cent glycerol solution did not result in a true solutioneven through 0.3 per cent protein concentration is quite low. It was found that a large amount of haemoglobin was floating on the surface of the foaming liquid. Thus most of it was not available for facilitation. This must be due to the large glycerol concentration in the particular solution (70 per cent) in which

haemoglobin was used. Further it was found at the later stages that the haemoglobin used was denatured. However, the large time separation factor α_{AB} for this system is quite appreciable (around 5).

The increase in α_{AB} with increase in glycerol concentration in the foaming liquid is most likely due to the sharp reduction in bubble breakage with time resulting from a radically increased foam stability. However, there are other factors here. An increase in glycerol concentration will also lead to a thicker foam membrane which will reduce gas permeability (of all gas species). Consider Table 4.1 and Table 4.2, the O_2 permeability as well as N_2 permeability decrease with increase in glycerol concentration from 50 per cent to and 70 per cent at low times. This is most likely attributable to thicker foam membranes. This phenomena was observed by Li [3] as well for liquid membranes separating liquid mixtures.

The change in the values of the gas permeabilities as well as separation factor with time is to be looked at from several directions. The data taken at low times will be affected by initial bubble breakage that takes place during bubble formation. This reduces α_{AB} as well as permeabilities because of contamination. Such is not the situation for large time with stable bubbles. In addition, as time proceeds the foam drainage in the bubbles will considerably reduce the foam membrane thicknesses leading to higher values of permeabilities. Table 4.2 and 4.3 demonstrate this. The increase in separation factor α_{AB}

with time can only be partially explained by lack of bubble breakage which takes place at the time of forming bubbles. An additional explanation is to be sought from the manner in which the term (dN_{AC}/dt) was calculated. This term was approximated by $(\Delta N_{AC}/\Delta t)$ and experimental values substituted to obtain its value. However, in the initial time period, the height variation becoming almost zero and any measurement error will be considerably magnified.

It is quite appropriate to compare the $\alpha_{O_2-N_2}$ values of this work with those available in literature for separation through flat liquid membranes. Cook and Tock [8], had obtained a value of 2.24-2.99 for $\alpha_{O_2-N_2}$ system with 2 weight per cent surfactant solutions in water. N.N.Li [11] had obtained a separation factor of 4 for O_2-N_2 separation through pure glycerol film. The present result of $\alpha_{O_2-N_2}$ varying between 3.4 to 5.8 is therefore understandable in such a context.

The results for CO_2-O_2 system as shown in Table 4.4 are similar with regard to increase in permeability with time. However, the separation factor decreases with time. In addition, the magnitude of this separation factor $\alpha_{CO_2-O_2}$ is around 8.2-6.7 which is smaller than that reported by Cook and Tock [8] (namely 19.9). The most likely reason for this behaviour is that a lot of CO_2 is likely to have been absorbed by the foaming liquid which was not in equilibrium with CO_2. Further, CO_2 permeabilities being higher, measurements have to be done quickly. This had

introduced unexpected errors since only 3.5 minutes were available for the experiment. If CO_2 were used as gas B after equilibriating the foaming liquid with it and O_2 were used to generate bubbles, some of these difficulties could have been avoided.

It must be clear from the results quoted and the discussion that a significant advance in gas separations is possible through foam liquid membranes. However, the present measurements of gas permeabilities through foam liquid membranes have the following inaccuracies:

1. Lack of simultaneous measurement of height reduction with time of a number of bubbles in any experiment,

2. Orsat gas analysis methods are slow and chromatographic methods are necessary.,

3. Sparger design should enable the generation of a monodisperse bubble population,

4. The foam membrane permeator column surface was improper resulting in difficulties for obtaining a sharp photograph.

CHAPTER 5

CONCLUSIONS

1. It is possible to make reasonable estimates of permeabilities of permanent gases through liquid membranes in the form of a foam liquid membrane and thereby determine the separation factors for separation of gas mixtures.

2. Foam stability is quite important in making such measurements accurately.

3. The selection of the gas system and the liquid for foam making must take into account gas absorption or prior gas-liquid equilibration.

4. Very high separation factors of around 5 are possible for the O_2-N_2 system with 70 per cent glycerol solutions whereas solid membranes have O_2-N_2 only in the range of 2-3. Thus continuous foam membrane separators are likely to become possible candidates for air separation as well as other separations.

5. Foam membrane gas separation processes with monolayer foam in the sheet form has been shown to be an altogether new approach in gas separations.

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CHAPTER 6

SUGGESTIONS FOR FUTURE WORK

1. More accurate methods for determining the composition of the gases in the continuous phase have to be devised. This may be done by means of a thermal conductivity detector a Gas-Liquid Chromatograph.

2. The surface of the glass column in which the foam is generated has to be smooth so that good photographs may be obtained.

3. A permanent stand for keeping the camera with special close up lens, has to be made.

4. Special lamps have to be used for uniform illumination of the bubbles to obtain a sharp photograph.

5. Provision has to be made for breaking the bubbles, inside the permeator and hence cleaning the apparatus. This can be achieved by keeping a metallic ring inside the glass column, which can be moved from outside.

6. The holes on the sparger should be made uniform and symmetrically to get uniform bubbles in a monolayer.

7. The simultaneous measurement of height reduction of several bubbles can be made with a movie camera.

8. Gas permeability measurements with A and B interchanged should be attempted.

9. Attempts should be made to obtain analytical solutions for the non-linear differential equations governing the systems.

10. With closer data points visa-a-vis time, better estimates of the first derivatives can be made.

11. Explore the separation of a gas mixture inside the bubbles with a rather impermeable gas on the outside.

12. The thesis can be extended to a continuous system as discussed by Didwania [5].

REFERENCES

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APPROXIMATIONS FOR PRESSURE CONDITIONS INSIDE AND OUTSIDE THE BUBBLES

$$P_{ij} - P_C = \frac{2\sigma}{r_j} \tag{2.7}$$

Here

σ = surface tension for glycerol = 63.4 dynes/cm

r_j = radius of the bubble = 0.5 cm (say)

$$\frac{2\sigma}{r_j} = \frac{2 \times 63.4}{0.5} = 253.6 \text{ dynes/cm}^2$$

$$P_C = 1.02 \text{ atm.} = 1.02 \times 76 \times 13.6 \times 980 = \varphi (10^6)$$
$$\text{dynes/cm}^2$$

Therefore $\frac{2\sigma}{r_j}$ is very small compared to P_C the outside phase pressure.

Hence $P_{ij} \simeq P_C$ $\qquad\qquad$ (2.8)

APPENDIX A.2.2

ESTIMATE OF MOLE RATIO OF SPECIES A IN BOTH PHASE AT
LARGE TIME

Approximate value of $N_{Ai}^{O} = 0.02$ moles

When the time is large,

approximate value of $N_{AC} = 0.011$ (say)

$$N_{Ai}^{O} - N_{AC} = 0.02 - 0.011 = 0.009$$

$$\frac{N_{AC}}{N_{Ai}^{O} - N_{ac}} = \frac{0.011}{0.009} = 1.2$$

$$\frac{N_{AC}}{N_{Ai}^{O} - N_{AC}} \simeq 1$$

<u>APPENDIX A.2.3</u>

<u>APPROXIMATION FOR EQUATION(2.33)</u>

$$\bar{v}(t) = \frac{\bar{\bar{v}}(0)}{2} \quad \text{(say)}$$

$$V = 10 \, N\bar{v}(0) \quad \text{(say)}$$

$$\underset{I}{N} + \underset{II}{\frac{V}{\bar{v}(t)}} = N + \frac{10 \, N\bar{v}(0)}{\bar{v}(0)/2}$$

$$I + II = N + 20H$$

Since the second term is 20 times larger than the first
it can be approximated as $N + \dfrac{V}{\bar{v}(t)} \cong \dfrac{V}{\bar{v}(t)}$

———

APPENDIX A.3.1

BASIS OF DESIGNING FOAM MEMBRANE PERMEATOR

From Fick's law

$$Q_A + \frac{A}{w} K_A P(x_{AA} - x_{AB})$$

(A.3.1)

Q_A = Flux of the gas A in (gm. moles/sec)

w = Film thickness (cms)

P = Pressure (Torrs)

K_A = Permeation constant $\left[\dfrac{\text{cm. gm. moles}}{\text{Sq. cm. Torrs sec}}\right]$

C_{AA} = Concentration of gas A on side A

C_{AB} = Concentration of gas A on side B

Knowing Q_A, P, K_A, w and concentration of A both inside and outside, A can be calculated. We now consider a gas like CO_2 or O_2 for estimating the surface area required. It has been observed that 50 per cent of CO_2 diffuses out from the bubbles within 3 min. from starting (5) with CO_2 inside and H_2 outside.

Now the volume of gas space above foaming liquid = 4330 cc

Volume of gas diffused $= (4330)4/100$

$= 173.2$ cc

gm.moles of gas diffused $= \dfrac{173.2}{22400}$ gm.moles

$$Q_A = \frac{173.2}{(22400)180} \frac{\text{gm.moles}}{\text{sec}}$$

Assume a film thickness (10) of 100 A°

$$w = (100)10^{-8} \text{ cm} = 10^{-6} \text{ cm.}$$

Pressure $= 1$ atm $= 760$ Torrs.

From (8), $K_A = (12.3) 10^{-9} \dfrac{cc. \ gm. \ moles}{sq. \ cm. \ Terrace}$

Suppose we assume $x_{AA} = 0.2$ and $x_{AB} = 0$

then $\qquad P_{AA} = 0.2(760)$ Torrs.

$\qquad P_{AB} = 0.$

Substituting in eqn.(A.3.I)

$$\frac{173.2}{22400(180)} = \frac{(12.3)10^{-9}(A)}{10^{-6}} \times 760(0.2)$$

$$A = \frac{173.2}{22400(180)} \times \frac{10^{-6}}{12.3 \ 760 \ 0.2 \ 10^{-9}}$$

$$= 0.2 \times 10^{-4} \ cm^2$$

Hence even for 10^{-2} cm thick bubbles, surface area needed is very little. For sake of convenience and to get ample gas for analysis we make the column of 65" dia. and 20" height. This will reduce the edge effects on bubbles and fairly wide area would be available. For Orsat analysis at least 4 or 5 cc of permeator gas would be available per 100 cc carrier gas (Phase B).

LAGRANGIAN INTERPOLATION FOR $\bar{h}(t)$

A model calculation of the Lagrangian Interpolation necessary for estimating $\bar{h}(t)$ is shown below.

For 70 per cent glycerol, 28 per cent H_2O and 2 per cent saponin solution, the r and h values at time t=5 min were obtained as follows:

$$r(cm) = 0.570 \quad 0.680 \quad 0.732$$
$$h(cm) = 0.265 \quad 0.393 \quad 0.513$$

From photographed data $\bar{r} = 0.590$ cm for 70 per cent glycerol system. The value of $\bar{h}(t)_{5 \text{ minutes}}$ corresponding to this value of $\bar{r}$ is to be interpolated from Lagrangian interpolation.

By Lagrangian interpolation formula

$$\bar{h}(r) = h_{1P0} + h_{2P1} + h_{3P_2} \tag{A.4.1}$$

The value P_o, P_1 and P_3 may be found by

$$P_o = \frac{(\bar{r}-r_2)(\bar{r}-r_3)}{(r_1-r_2)(r_1-r_3)}$$

$$= \frac{(0.596-0.68)(0.596-0.732)}{(0.570-0.68)(0.570-0.732)} = 0.641$$

Similarly P_1 and P_2 may be written as

$$P_1 = \frac{(0.596-0.57)(0.596-0.732)}{(0.680-0.57)(0.68-0.732)} = 0.618$$

and $\quad P_2 = \frac{(0.596-0.57)(0.596-0.68)}{(0.732-0.57)(0.732-0.68)} = -0.259$

These values when substituted in (A.4.1)

$$\bar{h}(0.596)_{5\text{minutes}} = 0.265(0.641)+(0.396)(0.618)-(0.513)$$
$$(0.259)$$
$$= 0.2727$$

MODEL CALCULATIONS FOR DETERMINING PERMEABILITY OF SPECIES A AND B

SYSTEM: O_2-N_2

FOAM LIQUID CONCENTRATION: 50 per cent Glycerol, 48 per cent H_2O

and   2 per cent Saponin.

Height of the column above bubble surface = 18.2 cm.

Diameter of the column = 17.0 cm

Volume of the space filled with N_2 = $17^2 \times 18.2 \times \pi/4$

= 4131.0 cc

Pressure in the continuous phase = 1.022 atm

(contains only N_2 to start with)

Moles of N_2 in the continuos phase at t = 0

= PV/RT

R = 82.06 atm/gm.moles ^{O}K

T = 308°K

Moles of N_2, N_{BC}^O = $\dfrac{1.022 \times 4131}{82.06 \times 308}$

= 0.167 gm.moles

Volume of O_2 sent in to form foam bubbles = 400 cc

Pressure of O_2 = 1.03 atm

Moles of O_2, N_{Ai}^O = $\dfrac{1.03 \times 400}{82.06 \times 308}$

= 0.0163 gm.moles

x_B^O = $N_{BC}^O/(N_{Ai}^O + N_{BC}^O)$

= 0.911

Radius of the average bubble from the photograph = 0.371 cms.

At time t=0 min, volume of the average bubble $\bar{v}(0) = h\,\bar{r}^2 \times 2/3$

$$= 0.1062 \text{ cc}$$

At time $t = 3$ min, volume of average bubble $\bar{v}(3) = 0.0797$ cc

Surface area of the average bubble $\bar{s}(t) =$

$$\bar{r}^2 + \frac{\bar{h}(t)\,\bar{r}}{(\bar{r}^2 h^2)^2} \, lh \, \frac{\bar{r}+(\bar{r}^2-\bar{h}^2)^{\frac{1}{2}}}{\bar{r}^2-(\bar{r}^2-\bar{h}^2)^{\frac{1}{2}}}$$

$$\bar{s}(3) = 0.7224 \text{ cm}^2$$

If we assume the change in pressure and volume in the continuous phase is negligible due to diffusion of species A and B, the total moles remain the same.

Concentration of O_2 at t=3 min = 6.5 per cent

$$N_{AC}(3 \text{ min}) = 0.065 \times 0.167 = 0.0108 \text{ gm.moles}$$

$$\frac{dN_{ac}}{dt} = \frac{RT \, PermA \, (N_{Ai}^0 - N_{AC}(t))}{\bar{v}(t)/\bar{s}(t)}$$

$$= 0.0036 \text{ gm. moles/min}$$

$$\frac{\bar{v}(3)}{\bar{s}(3)} = 0.0797/0.7224 \text{ cm} = 0.110 \text{ cm.}$$

$$N_{Ai}^0 - N_{AC}(3 \text{ min}) = 0.0163 - 0.0108 = 0.0055 \text{ gm.moles}$$

$$Perm \ A = \frac{0.0036 \times 0.0797}{0.7224 \times 82.06 \times 308 \times 0.0055}$$

$$= 2.8 \times 10^{-6} \frac{\text{gm. moles}}{(\text{atm})(\text{cm}^2)\text{min}}$$

$$\frac{d\bar{v}}{dt} = RTS \, (Perm \ B - Perm \ A) \, x_B^0 - Perm \ B\frac{(1-\bar{v}(0))}{\bar{v}(t)}$$

$$= \bar{r}^2 \, \frac{d\bar{h}}{dt} \, 2/3$$

$$= \pi \, 0.371)^2 \, \frac{(0.3685-0.2765)}{0-3} \quad (2/3)$$

$$= -0.0088 \text{ cc/min.}$$

$$\bar{v}(0)/\bar{v}(3) = 0.1062/0.0797 = 1.3341$$

$$-0.0088 = (82.06)(308)(0.7224)((\text{Perm B}-\text{Perm A})0.911 -$$
$$\text{Perm B }(1-1.3341))$$

i.e. , 1.2451 Perm B-0.911 Perm A $= -0.48 \times 10^{-7}$

$$\text{Perm A} = 2.8 \times 10^{-6} \text{ gm. moles/(cm}^2)(\text{atm})(\text{min}).$$

$$\text{Perm B} = 1.66 \times 10^{-6} \text{ gm. moles/cm}^2 \text{ atm. min.}$$

Separator factor $\alpha_{AB} = \dfrac{\text{Perm A}}{\text{Perm B}} = 2.8 \times 10^{-6}/1.66 \times 10^{-6} = 1.687.$

NOMENCLATURE

The following are most commonly used symbols in the theis.

n_{Aij} = moles of species A inside jth bubble.

n_{Bij} = moles of species B inside jth bubble

N_{AC} = moles of A outside the bubbles (continuous phase)

N_{BC} = moles of B in continuous phase

N = total number of bubbles in the monolayer

P_c = total pressure outside the membrane in the continuous phase

P_{ij} = pressure inside jth bubble

S_j = surface area of jth bubble

N_{TC} = total number of moles of gases in the continuous phase

n_{Tij} = total number of moles of all gases inside the jth bubble

PermA= permeability of species A

PermB= permeability of species B

R = gas constant

T = temperature

V = volume of the space above liquid level

v_j = volume of the jth bubble

σ = surface tension

r_j = radius of the jth bubble

S_T = total surface area of all the bubbles

$\bar{n}_{Ai}$ = moles of A inside the average bubble

$\bar{n}_{Bi}$ = moles of B inside the average bubble

$\bar{v}$ = volume of an average bubble

$\bar{s}$ = surface area of an average bubble

N_{Ai}^{O} = total moles of A inside the bubbles at time t=0.

p = partial pressure

$\bar{r}$ = radius of the average bubble

$\bar{h}(t)$ = height of the average bubble at any time t

α_{AB} = separation factor

Subscripts

A = species A

B = species B

i = inside the bubbles

j = jth bubble

c = continuous phase

T = total

Superscripts

$-$ = average

o = values at time t=0